

**"A PROCESS FOR THE MANUFACTURE OF BIO-RELEASE
IRON -MANGANESE RELEASE FERTILIZER"**

Field of invention

This invention relates to a process for the manufacture of bio-release types of slow-release iron-manganese fertilizer compounds wherein these micronutrients are water insoluble but are nevertheless available for plants.

Background of invention : Prior Art And Drawbacks

Iron and manganese fertilizers are widely used in many parts of the world particularly in soils of high pH, such as the black soils. They are also widely used in horticultural and cash crops to improve yields and quality of produce. The compounds most popularly used for correcting deficiencies of iron and manganese in crops are ferrous sulphate and manganous sulphate (J.J. Mortvedt, P.M. Giordano & W.L. Lindsay, 1972, Micronutrients in Agriculture, Soil Sci. Soc. Am., Madison). Chelated forms of these micronutrients, e.g., iron-EDTA, and manganese -EDTA compounds are also in use as liquid sprays (V. Saucheli, 1967, Chemistry and technology of fertilizers, Reinhold, New York; G.H. Collins, 1955, Commercial fertilizers, Mc-Graw Hill, New York).

There are, however, several drawbacks in the use of such soluble compounds as fertilizers of iron and manganese, e.g., leaching losses, chemical transformation losses, ground water contamination, etc. This results in excess dosages which are often several times the actual crop uptake, leading to poor fertilize-use efficiency

Moreover, such wastages also affect the economics of iron and manganese fertilizer, thereby discouraging their widespread usage.

In an attempt to overcome these shortcomings, slow-release fertilizers incorporating iron and manganese have been prepared. One such type is the fertilizer based on phosphate glasses known as frits. Frits are prepared by fusing sodium, potassium or ammonium dihydrogen phosphates together with micronutrient salts at temperatures between 800⁰ and 1400⁰C and then rapidly quenching the melt to produce a glass (G.J. Roberts 1973, Am. Ceram. Soc. Bull. Vol 52, p383; *ibid*, *idem*, Vol 54, p1069; Austrian Patent No 326160 of 1975; US Patent No. 3574591 of 1971; US Patent No 2713536 of 1974).

The major disadvantage of the phosphate glass frits is that the availability of the nutrients is by slow hydrolysis of the glass and is highly dependent on the soil (pH, moisture content, temperature, etc.,) and on the crop (rate of growth, physiological factors, variety, etc). Consequently, where nutrient release by hydrolysis does not match plant uptake, the fertilizer is not effective. Moreover, the high temperatures involved in the synthesis of frits together with the corrosive conditions make these materials fairly expensive and unsuitable for general use.

Another type of phosphate based water insoluble fertilizer is the metaphosphate. Metaphosphates of calcium and potassium together with micronutrients have been proposed (SI Volfkovich, 1972, J Appl. Chem. (USSR) Vol 45, p2479). A Russian

patent (SU 1270148 of 1986) describes the production of mixed metaphosphates based fertilizers produced at 500⁰-880⁰C. Drawbacks in the use of metaphosphates as fertilizers are similar to those with the frits. Metaphosphates may be more insoluble and hydrolyse even slower, producing compounds with very poor nutrient availability. Metaphosphates of the heavy metals are extremely insoluble and of little use as fertilizers.

An additional type of slow-release fertilizer has been produced in which the micronutrient ions are in a chemical form wherein they are insoluble but also plant available. These belong to the bio-release types of slow-release fertilizers. The processes for producing such phosphate based zinc and copper fertilizers are described in two Indian patents (Nos 172800 of 1990 and 177205 of 1991). The chemistry of zinc and copper phosphate polymerisation and the chemical nature of these fertilizers have also been described (SK Ray, C Varadachari & K Ghosh, 1993, Ind. Eng. Chem. Res. Vol. 32, p. 1218; SK Ray, C Varadachari & K Ghosh, 1997, J. Agric. Food Chem., vol. 45, p. 1447). A new patent (C. Varadachari, Indian Patent Application No. 10/CAL/99) describes the processes for production of slow-release fertilizers and describes methods for assessing limits of polymerisation.

Objectives of the invention

An objective of this invention is to propose a process for the manufacture of bio-release iron-manganese fertilizer having all the advantages of slow-release fertilizers together with the added benefit of high nutrient availability.

Another objective of this invention is to provide a combined nutrient source of iron and manganese in a single compound. Since deficiencies of iron and manganese in soils always occur together, therefore, a fertilizer providing both nutrients would be more beneficial for crop growth.

The third objective of this invention is to provide a bio-release source of ammonium, magnesium and phosphorus, all of which are essential plant nutrients.

Still another objective of this invention is to propose a process for the manufacture of bio-release iron-manganese fertilizer, wherein only a single heating stage is required and polymerisation temperatures are lower than all previous processes.

Yet another objective of the invention is to provide a processes for producing slow-releasing, water insoluble, iron-manganese fertilizers that will show good bio-availability of the nutrients and thus provide an effective source of iron and manganese for plants.

A further objective is to provide processes, which offer substantial improvements over earlier processes, in providing a combined micronutrient source and also in terms of energy requirement

Description of the invention

According to this invention, there is provided a process for the preparation of water insoluble bio-release iron-manganese fertilizer, which comprises (a) heating phosphoric acid with a mixture of (i) source of iron oxide such as goethite and hematite, (ii) pyrolusite and (iii) one or more basic compound(s) selected from oxide(s) or carbonate(s) of magnesium, calcium, sodium and potassium, (b) neutralisation followed by drying and pulverisation.

When oxide of iron [goethite i.e., $\text{FeO}(\text{OH})$ or hematite i.e., Fe_2O_3], pyrolusite (MnO_2) and a basic compound (oxides or carbonates of magnesium, calcium, sodium or potassium) are heated with phosphoric acid, reaction occurs to form the dihydrogen phosphates of the metal ions, which subsequently polymerise to form iron manganese polyphosphate.

Removal of free water from the system by heating facilitates the reactions.

Vacuum facilitates the reaction by speeding up the removal of water.

Polymerisation is allowed to continue till a product of optimum chain length is formed as determined by its chemical properties. This polyphosphate product is a

viscous, acidic liquid. When neutralised with magnesia or ammonia, a light coloured suspension is formed which can be dried and ground to a free flowing, non-hygroscopic product.

Iron-manganese fertilizer

The starting materials are yellow oxide of iron, i.e., goethite, which may contain up to 62.8% Fe or red oxide of iron, i.e., hematite containing up to 69.9 % Fe, pyrolusite which may contain up to 63% Mn, magnesia which may contain up to 60.3 % Mg or magnesium carbonate which may contain up to 28.8 % Mg and phosphoric acid containing not more than 60% P_2O_5 .

The raw materials, goethite and pyrolusite, are in such proportions that molar ratios of Fe : Mn = 1 : 0.51. Although higher or lower ratios ranging from Fe : Mn = 1 : 0 to 0 : 1 may be used, this ratio of 1 : 0.51 is considered most suitable from the point of view of crop requirements. Magnesia is added in the proportion Fe : Mg (molar ratio) = 1 : 1.15.

With lower ratios of Mg, desirable properties are not obtained; higher ratios of Mg do not result in any particular improvement of the product or the process. Product remains tolerable with Fe: Mg molar ratios ranging from 1 : 0.6 to 1 : 1.75. However, a Fe : Mg molar ratio = 1 : 1.15 is optimum. The Mg compound may also be replaced with a Ca compound. Thus dolomite ($CaCO_3 \cdot MgCO_3$) or

limestone (CaCO_3) may be used. The molar proportion of Fe : cation is preferably 1 : 1.15 although ratios ranging from 1 : 0.575 to 1 : 1.725 may also be used. Alternatively, sodium or potassium bases may be used. In such case, the Mg is replaced by equivalent amounts of Na or K.

The molar ratio of Fe : Na/K = 1 : 2.3 is at the optimum level. The amount of phosphoric acid added is such that all the Fe, Mn and Mg as well as impurities in the reaction mixture are converted to the dihydrogen phosphates. Thus, the Fe : Mn : Mg : P molar ratios used are 1 : 0.51 : 1.15 : 7.34. Lower ratios of P will result in incomplete reaction of the oxides. Higher levels of P at any level may be used but is of no particular advantage. On the contrary, this will result in excess acidity in the product that will require more bases for neutralisation.

The reactants are taken in an acid-proof brick lined reactor vessel. All the reactants are mixed together and heated at 200°C . Application of vacuum at this stage facilitates the reaction. As the reaction progresses, the colour changes from dirty yellow or red (depending on the colour of the starting material); it deepens and ultimately becomes almost black. Any temperature above 160°C can be used for the reaction; however, temperatures of $200\text{--}250^\circ\text{C}$ give the optimum results. Temperature of liquid itself, however, remains at around 140°C . Pre-heating at lower temperatures is not required since dissolution of solids occurs during the period when liquid temperature slowly increases by absorption of external heat. As

the system absorbs heat, initially, dihydrogenphosphates of iron, manganese and magnesium are formed. With further absorption of heat, polymerisation of the phosphates occurs with formation of iron manganese magnesium polyphosphate. By eliminating the initial heating period, the reaction is much faster without any loss of product quality. The reaction can be followed by observing the changes in colour, density and viscosity of the liquid. At the end of the reaction period the liquid is almost black in colour. Density changes are also useful to obtain the end-point of reaction. Density of the liquid shows a sharp increase near the end-point; it is 1.97 g/ml (in the hot state, at around 140⁰C) in the product having the desired polymerisation. Viscosity changes are also sharp; viscosity increases from around 19 centipoise to 43 centipoise (at a temperature of about 140⁰C) at the end-point. The polyphosphate is a flowable liquid when hot but when cooled to room temperature, it becomes a thick, highly viscous material. After the end-point of reaction, if heating is further continued, the liquid becomes highly viscous and hair-like strands are formed, which solidify on cooling.

Further testing of the product is done by taking a small portion, neutralising with ammonia to pH 5.0-7.5. Optimum pH for neutralisation is pH 5.6-6.0. The product is tested for its solubility in 0.33M citric acid and 0.005M DTPA (diethylene triamine penta acetic acid). The product of desired degree of polymerisation is almost completely soluble in these reagents within 60 min.

Higher polymerised product will leave an insoluble residue and is not a desirable material. Lower polymerised products may contain unreacted black particles (pyrolusite).

The polyphosphate, at the desired level of polymerisation, is a flowable liquid. It is poured into a container, allowed to cool to room temperature and subsequently neutralised with a basic material. Ammonia solution is preferred because time requirement for neutralisation reaction is faster compared to solid bases like magnesia, magnesium carbonate, lime, etc. However, any such basic material may be used. Optimum pH for neutralisation is 5.5- 6.5. If too little base is added, the finished product will tend to become hygroscopic. Solubility in citrate and DTPA solutions will also be lower. Addition of too much of base offers no particular advantage and will also make the product more insoluble in citrate and DTPA solutions. After neutralisation, the dark blackish product changes colour to a light gray material. This is dried at temperatures $< 100^{\circ}\text{C}$, preferably at $60\text{-}80^{\circ}\text{C}$. It is then ground and sieved, preferably through 100 mesh.

This invention provides a substantial improvement over previous processes for the production of combined iron-manganese fertilizers. In this process the initial reaction stage to produce a homogenous mixture is eliminated. A single stage reaction, at temperatures of 160°C or higher is sufficient to produce the polyphosphate. Thereby total time of reaction is reduced. This has been possible

because of addition of Mg^{2+} ions, which helps in more rapid and easier dissolution of pyrolusite. The polymerised end product remains in a liquid state, which makes material handling and transfer easier. Process control is also simplified since density and viscosity of the liquid can be continuously monitored and thereby the end-point of reaction can be readily detected.

Accordingly, this invention provides a process for the production of multinutrient bio-release fertilizer of iron-manganese. All existing slow-releasing fertilizers of the micronutrients have nutrient release controlled by hydrolysis or diffusion mechanisms. The new bio-release forms have a superior nutrient supply mechanism, which is similar to that from the soil nutrient storehouse. Thus, in this Fe-Mn fertilizer the nutrients are present in water insoluble but simultaneously in a plant available form. The fertilizers are also non-toxic, non-hygroscopic, environment friendly, easy to apply and exhibit improved fertilizer use-efficiency.

The main advantage of this process is the significant improvement in energy use by converting a two-stage process to a single stage process. Another advantage is improvement in process control, by combining iron, manganese and magnesium, which produces liquid polyphosphates whose solubility characteristics are less sensitive to the degree of polymerisation. This is more difficult in iron-manganese systems in the absence of magnesium. Yet another advantage of this invention is the easy technique of obtaining the end-point of reaction by continually monitoring

density or viscosity of the liquid. Lastly, the process is simpler and requires less energy inputs than all previous processes.

The invention will now be explained in greater detail with the help of the following non-limiting examples.

Example 1

Phosphoric acid containing 60 % P_2O_5 is taken in a glass beaker. To 145 g of the acid, 16 g of goethite (containing 62 % Fe), 7.86 g pyrolusite (containing 63 % Mn) and 8.2 g magnesia (containing 60.3 % Mg) is added and stirred. The colour of the mixture at this stage is dirty yellow. The beaker is then placed in a furnace set at 200°C. Much frothing occurs as the polymerisation proceeds. After 45 min of heating, the beaker is taken out of the furnace. At this stage the colour of the liquid is almost black. A small amount is taken for density and viscosity measurements of the hot liquid. These values are about 1.97 g/ml and 43 centipoise respectively. Another portion is neutralised with ammonia to pH 5.6 and tested for its solubility in 0.33M citric acid. The desired product gives an almost clear solution within 60 min. Materials, which are much too polymerised or too little polymerised leave a residue.

The polyphosphate, when hot, is a flowable liquid. It is allowed to cool to room temperature whereupon it becomes a viscous liquid. 85g of magnesium oxide is

added to the polyphosphate with mixing. The pH of the product is, thus, raised to about 5.6. Its colour changes to very light gray. It is then dried in an oven at 80°C, ground in a mortar and sieved with 100 mesh sieve. The fertilizer contains 5.4% Fe₂O₃, 2.7% MnO₂, 18.4% MgO and 34.5% P₂O₅.

Example 2

12 kg of commercial phosphoric acid containing 58.5% P₂O₅ is taken in an acid-proof brick lined reactor vessel with a stirrer. To this, 732 g pyrolusite (containing 51.6% Mn), 1212g goethite (containing 62% Fe) and 1836g magnesium carbonate (containing 20.5% Mg) are added, one after another. The suspension is stirred. Frothing occurs due to the presence of carbonate. The vessel is closed, stirring is continued and heating is started with the temperature set at 200°C. Density and viscosity of the liquid are continuously recorded and heating is stopped as the appropriate stage is reached (density of 1.97g/ml and viscosity of around 43 centipoise). For this quantity of reactants 90 min heating is required at 200°C. The liquid is poured out into a stirrer. It is allowed to cool to nearly room temperature then 11 litre ammonia solution (25% ammonia) is slowly added with continuous stirring. A sample is taken and tested for its pH, which should be around 5.6-6.0. The suspension is poured out into trays and dried in an oven at 80°C. It is finally ground to a 100 mesh size.

The fertilizer contains 5.5 % Fe, 2.8 % Mn, 16 % P, 3 % Mg and 11 % N. It is tested to be almost completely soluble in 0.33M citric acid and 0.005M DTPA.

Plant growth trials with this fertilizer were done in black cotton soil with rice, spinach and chillies as test crops. Rice produced a 45% increase at 2 kg/ha Fe and 1 kg/ha Mn as the bio-release fertilizer. Chillies gave a 179% higher yield at the same dose of bio-release fertilizer. The residual effect of the fertilizer produced a 51% increase in yield of spinach.

Example 3

135 g commercial phosphoric acid (containing 58.5 % P_2O_5) is mixed with 16g hematite (containing 50.5 % Fe and 2.87 % Al), 7.84g pyrolusite (containing 51.6 % Mn) and 19.7g magnesium carbonate (containing 20.5 % Mg). The reactants are taken in a borosilicate glass beaker, stirred and kept in a muffle furnace set at 250°C. After 20 min the beaker is removed from the furnace. A sample is neutralised with ammonia up to a pH of 5.6 and its solubility in 0.33 M citric acid is tested. It is almost completely soluble. A light gray product is formed which is dried at 70°C in an oven. The dried material was powdered and sieved through 100 mesh.

Example 4

This procedure is essentially the same as described in example 1 except in the order of addition of reactants. Here phosphoric acid is taken in a beaker, pyrolusite is added to it and the mixture is heated at 200⁰C for 10 min. The beaker is removed from the furnace and goethite and magnesium are added with stirring. The reactants are again heated at 200⁰C for 30 min. The end product is tested as described in example 1; the finished product is also obtained as described therein.

Example 5

This is essentially the same as example 2 except that at the neutralisation stage, 11 kg potassium carbonate is used instead of ammonia solution.

Example 6

This is essentially the same as example 1 except that at the initial reaction stage dolomite 22.5g (containing 21% Ca and 13% Mg) is added as an ingredient, instead of magnesium carbonate. The mixture is heated at 250⁰C for 40 min to obtain the desired level of polymerisation.

Example 7

This is essentially the same as example 1 except that at the initial reaction stage 31.8g sodium carbonate (containing 29 % Na) is used instead of magnesium carbonate. The mixture is heated at 250⁰C for 100 min to obtain the desired level of polymerisation.

Example 8

This is essentially the same as example 1 except that 8g sodium hydroxide (containing 57.5% Na) is used instead of magnesium carbonate.

Example 9

This is essentially the same as example 1 except that 90g magnesium carbonate (containing 28 % Mg) is used for neutralisation instead of ammonia.

Example 10

This is essentially the same as example 1 except that at the initial reaction stage calcium carbonate 20.7 g (containing 40 % Ca) is added as an ingredient, instead of magnesium carbonate. The mixture is heated at 250⁰C for 50 min to obtain the desired level of polymerisation.